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Racemic α-Methyl-*β*-propiolactone Polymerization by Organometallic Catalyst Systems

Jin Xu,† Stephen P. McCarthy, and Richard A. Gross*

NSF Biodegradable Polymer Research Center, University of Massachusetts Lowell,
One University Avenue, Lowell, Massachusetts 01854

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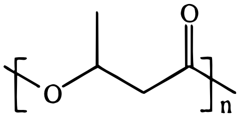
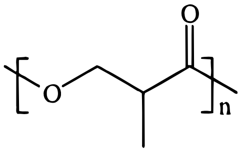
ABSTRACT: Polymerization of racemic α-methyl-*β*-propiolactone (MPL) was carried out using Zn-, Sn-, La-, Y-. and Al-based organometallic catalysts. It was found that $Zn(C_2H_5)_2/H_2O$ (1/0.6), $(^nC_4H_9)_2Sn(OCH_3)_2$, $Al(O^iC_3H_7)_3$, and $(C_2H_5)_2AlOC_2H_5$ produced atactic poly(α-methyl-*β*-propiolactone) (PMPL), whereas $(^nC_4H_9)_3SnOCH_3$ and $Y(O^iC_3H_7)_3$ formed PMPL of low isotacticity with isotactic (i) diad fractions between 0.53 and 0.56. Since the Sn-based catalysts were syndioregulating for *β*-methyl-*β*-propiolactone (BL) polymerizations, placement of the lactone methyl substituent at the α- instead of the *β*-position alters steric interactions between the incoming monomer and the Sn catalyst−chain end so that syndioaddition is no longer preferred. Isobutylaluminoxane (IBAO) produced a PMPL sample that can be separated by acetone into two fractions: an acetone-insoluble (AI) PMPL fraction of high isotacticity (i-diad fraction 0.85) and high molecular weight (M_n = 662 000 g/mol) and an acetone-soluble (AS) PMPL fraction of low isotacticity (i-diad fraction 0.57) and low molecular weight (M_n = 6740 g/mol). Chain stereosequence analysis at the triad level was performed by carbon (^{13}C) nuclear magnetic resonance at 75.4 MHz for PMPL products from IBAO catalysis. Excellent agreement was found between the experimental results and those calculated by the enantiomorphic-site model, suggesting that the configuration of the adding monomer was primarily controlled by the configuration of the catalytic sites. The AI fraction was highly crystalline based on DSC analysis (peak melting temperature 123 °C, enthalpy of fusion 16.3 cal/g). Methylaluminoxane (MAO) gave distinctly different results than IBAO-catalyzed MPL polymerization. Specifically, the number or activity of catalytic sites that lead to highly isotactic PMPL was less for MAO than for IBAO. For the polymerization of both BL and MPL, IBAO catalysts appear to function similarly so that at least two types of catalytic sites are present which produce a highly isotactic fraction with high molecular weight and a low isotacticity fraction with low molecular weight.

Introduction

Previously, we reported that optically active poly(α-methyl-*β*-propiolactone) (PMPL) stereoisomers can be obtained by a two-step chemoenzymatic route.[1] This was accomplished by using the lipase PS-30 from *Pseudomonas fluorescens* to resolve racemic α-methyl-*β*-propiolactone (MPL). The polymerization of 93% (*R*)-MPL resulted in a PMPL product that was highly crystalline (>73%), melted at 131 °C, and had an enthalpy of fusion of 22.0 cal/g.[1] The direct enzyme-catalyzed polymerization of racemic MPL was also accomplished using the lipase PS-30 to obtain (*S*)-enriched PMPL.[2] This latter method demonstrated that enzymes can be used to catalyze stereoelective ring-opening polymerization. From comparisons of PMPL and poly(*β*-hydroxybutyrate) (PHB) stereoisomers[3,4] with similar enantiopurities, it was concluded that both PHB and PMPL have considerable tolerance to stereochemical impurities so that they can crystallize at relatively low isotacticities and that PMPL can be prepared with a similar range of melting temperatures as PHB by appropriate variation in chain enantiopurity.[1] Rapid crystallization of PMPL while quenching from the melt and during second heating scans indicates that highly stereoregular PMPL may have desirable crystallization kinetics.[1] Interest in the chemical synthesis of PHB by the ring-opening polymerization of *β*-methyl-*β*-propiolactone (BL) was stimulated by the fact that PHB is synthesized in nature by a large number of bacteria.[5−8] Natural origin PHB is perfectly isotactic by virtue of the fact that the repeat units are all of the (*R*) stereochemical configuration.[5−8] Studies on PHB and related microbial polyesters have shown them to be exciting candidates for applications as biodegradable materials [9] as well as many other biotechnological products.[10] Since PMPL and PHB are closely related in structure, differing only in the position of the methyl substituent groups (see structures below),



PHB



PMPL

it is interesting to consider whether PMPL may possess similar or possibly superior properties relative to PHB. The stereospecific polymerizations of racemic BL to prepare isotactic,[11−16] syndiotactic,[17−19] and atactic PHB[3,13,20] using various organometallic catalysts have been well documented. In contrast, to our knowledge, no work has been carried out to evaluate what classes of organometallic catalysts are useful for MPL polymerization and the extent to which these catalysts will lead to stereospecific polymerizations. In this paper, the polymerization of racemic MPL using a wide range of organometallic catalyst systems was undertaken. Relevant previous work with the catalysts of interest herein is presented below.

$Zn(C_2H_5)_2/H_2O$ has been shown to be an effective catalyst for the polymerization of racemic BL to form atactic PHB, where chain propagation closely approxi-

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* Corresponding author.

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mates a statistically random mechanism.[3,13] BL polymerizations proceed via acyl (carbonyl−ring oxygen) cleavage, and the configuration of monomer stereocenters upon conversion to polymer repeat units is maintained.[21] Early work demonstrated that this catalyst system is effective for the ring-opening polymerization of racemic propylene oxide to prepare predominantly isotactic polyethers.[22]

Similar to the $Zn(C_2H_5)_2/H_2O$ catalyst system, yttrium 2-methoxyethoxide is a very active catalyst for the ring-opening polymerization of racemic BL.[20] The polymerization in toluene at 20 °C showed some characteristics of a "living" system, and the product formed was atactic PHB, suggesting that chain propagation was approximately random. Lanthanide and yttrium alkoxides have also been found to be active for the living ring-opening polymerization of lactide and ϵ-caprolactone.[23−25] However, the potential of lanthanide-based catalyst systems to be stereoregulating with respect to chiral lactone polymerizations has not been explored.

$(^nC_4H_9)_3SnOCH_3$ and $(^nC_4H_9)_2Sn(OCH_3)_2$ are able to catalyze the ring-opening polymerization of racemic BL in bulk to form predominantly syndiotactic PHB.[17,18] For example, PHB obtained from the polymerization of racemic BL using $(^nC_4H_9)_2Sn(OCH_3)_2$ as the catalyst at 60 °C for 2 days has a syndiotactic (s) diad fraction of 0.63.[18] These Sn-based catalysts were also found to be active for the polymerization of ϵ-caprolactone, L,L-lactide, and β-propiolactone.[26,27]

$Al(O^iC_3H_7)_3$ catalyzes the living polymerization of ϵ-caprolactone, lactide, and cyclic anhydrides.[28−32] The polymerization proceeds through a coordination−insertion mechanism. It has also been shown that $Al(O^iC_3H_7)_3$ is active for the polymerization of optically active β-(1,1-dichloroalkyl)-β-propiolactones with retention of monomer configuration. β-(1,1-Dichloroethyl)-β-propiolactone was polymerized according to a living mechanism. However, as the size of the β-alkyl group increased from methyl to butyl, the polymerizability of the lactone decreased substantially.[33] However, $Al(O^iC_3H_7)_3$ and $(C_2H_5)_2AlOC_2H_5$ have not been explored for the polymerization of other chiral lactones such as BL. Moreover, the stereoregularity of these catalysts has not been well established.

Aluminoxanes are products of the reactions between trialkylaluminum (R_3Al) and water. It is widely believed that the catalysts contain linear oligomers of different lengths as well as other components such as cyclic and cage compounds of different sizes.[15,16] The stereoregularity and reactivity of aluminoxane catalysts for the polymerization of racemic BL largely depend on the catalyst composition (ligand structure, Al/water ratio) as well as precise details of the preparative method. It was found that aluminoxane catalysts having more bulky alkyl groups are more effective in forming highly isotactic PHB. The effectiveness of the aluminoxanes for forming isotactic PHB was reported to be in the following order: isobutylaluminoxane (IBAO) > ethylaluminoxane (EAO) > methylaluminoxane (MAO).[15] PHB formed from aluminoxane-catalyzed polymerization of racemic BL usually has a broad molecular weight distribution and can be separated into highly isotactic and atactic fractions by acetone extraction. The isotactic fraction has high molecular weight and is crystalline, whereas the atactic fraction has a relatively lower molecular weight and is amorphous.[14−16,34]

In this paper, we report the results of racemic MPL polymerizations using $Zn(C_2H_5)_2/H_2O$ (1/0.6), $(^nC_4H_9)_3SnOCH_3$, $(^nC_4H_9)_2Sn(OCH_3)_2$, $Al(O^iC_3H_7)_3$, $(C_2H_5)_2AlOC_2H_5$, $Y(O^iC_3H_7)_3$, IBAO, and MAO as catalysts. Polymerizations were generally conducted at 60 °C for specified time periods and monomer-to-catalyst ([M]/[C]) ratios. Yields of PMPL as a function of polymerization conditions were determined. The average molecular weights and dispersities of the PMPL products were measured by gel permeation chromatography (GPC), and stereosequence fractions were analyzed by ^{13}C nuclear magnetic resonance (NMR). When appropriate, products were fractionated and analyzed by differential scanning calorimetry (DSC), GPC, and ^{13}C NMR. From this work, the potential utility of important classes of organometallic catalyst systems for MPL polymerization and the extent to which they are stereoregulating were determined.

Experimental Section

Materials. Racemic α-methyl-β-propiolactone (MPL) was synthesized and purified as reported previously.[1] $(^nC_4H_9)_3SnOCH_3$, $(^nC_4H_9)_2Sn(OCH_3)_2$, $Al(O^iC_3H_7)_3$, $(C_2H_5)_2AlOC_2H_5$ (25 wt % in toluene), and $Zn(C_2H_5)_2$ were purchased from Aldrich (purity >98%) and were used as received. $Y(O^iC_3H_7)_3$ and $La(O^iC_3H_7)_3$ were purchased from Johnson Matthey Electronics (purity >98%) and were used as received. For $Y(O^iC_3H_7)_3$, solutions were prepared (6.67 and 47.1 wt %) in dry toluene (distilled twice from CaH_2). Isobutylaluminoxane (IBAO, 3.62 Al wt % in heptane) and methylaluminoxane (MAO, 7.5 Al wt % in heptane) were purchased from Akzo Nobel Chemicals, Inc., and were used as received.

Preparation of $Zn(C_2H_5)_2/H_2O$ (Mole Ratio = 1:0.6) Catalyst. The procedure followed is a modification of that previously described[3,21] and is summarized below. To a silanized and flame-dried 100-mL Schlenck tube were charged 60 mL of dry 1,4-dioxane (distilled from CaH_2 and stored under Ar) and 14.0 mL of $Zn(C_2H_5)_2$ (neat; 136.6 mmol) via syringe under an argon atmosphere. After cooling the resulting solution in an external ice−water bath, 1.50 mL (83.3 mmol) of double-distilled deoxygenated H_2O was added slowly over a period of approximately 1 h while maintaining vigorous magnetic stirring. After another 40 min, the ice bath was removed and the temperature was equilibrated to ambient conditions. A clear light-yellow solution was formed along with a yellow precipitate. The clear solution was used as the catalyst.

Preparation of Poly(α-methyl-β-propiolactone) (PMPL). In the case of liquid catalyts (Zn, Sn, Y, $(C_2H_5)_2AlOC_2H_5$, MAO, and IBAO catalysts), racemic MPL (1 g) was added via syringe under argon atmosphere to a 5-mL ampule which was flame dried while purging with argon. The ampule containing the monomer was then frozen in an acetone−dry ice bath followed by removing the ampule from the bath. Immediately after the MPL liquified (<−25 °C), the catalysts in amounts specified below were added via syringe and the ampule contents were vortexed to mix. The mixtures were degassed by two freeze−pump−thaw cycles prior to sealing. The polymerizations were then carried out by placing the ampules either in an oil bath at 60 °C or a freezer (−20 °C) for specified time periods (see Table 1). In the case of solid catalysts (La and $Al(O^iC_3H_7)_3$ catalysts), the catalysts were transferred to flame-dried ampules (see above) in a dry bag while purging with dry argon, followed by the addition of monomer, freeze−thaw cycles, and ampule sealing. The workup procedures involved opening the sealed ampules, adding approximately 5 mL of chloroform to dissolve the reaction mixture contents, and precipitation of the product into 100 mL of methanol (polymerizations by Zn- and Sn-based catalysts) or petroleum ether (bp 35−60 °C, for polymerizations by La-, Y-, and Al-based catalysts). After storing the mixtures at room temperature for several hours and then at −20 °C for ~16 h, the insoluble material was separated by either centrifugation (8000 rpm, products pre-

Table 1. Yield, Molecular Weight and Isotatic (i) Diad Content for PMPL Products Obtained from Racemic MPL Polymerization using Various Organometallic Catalyts

catalyst	[M]/[C][a]	temp °C	polym time, days	yield, %	M_n $(M_w/M_n)^b \times 10^{-3}$ (g/mol)	i-diad fraction[c]
$Zn(C_2H_5)_2/H_2O$ (1/0.6)	*d*	60	7	55[e]	22.2 (1.44)	0.51
$(^nC_4H_9)_3SnOCH_3$	100	60	7	24[e]	15.9 (1.26)	0.55
				54[f]	4.36 (1.53)	0.56
$(^nC_4H_9)_2Sn(OCH_3)_2$	100	60	7	12[e]	9.59 (1.31)	0.51
				69[f]	2.66 (1.50)	0.50
$La(O^iC_3H_7)_3$	50	60	21	0[g]		
$Y(O^iC_3H_7)_3$	50	60	3	94[g]	3.02 (1.27)	0.53
$Y(O^iC_3H_7)_3$	500	60	41	87[g]	11.0 (1.63)	0.54
$Y(O^iC_3H_7)_3$	1500	60	28	0[g]		
$Y(O^iC_3H_7)_3$	50	-20	3	55[g]	1.81 (1.51)	0.53
$Al(O^iC_3H_7)_3$	50	60	3	95[g]	2.40 (1.40)	0.50
$(C_2H_5)_2AlOC_2H_5$	50	60	3	88[g]	6.50 (1.71)	0.50
MAO[h]	50	60	3	52[g]	4.74 (2.53)	0.55
IBAO[h]	50	60	3	58[g]	6.85 (2.78)/641 (1.40)[i]	0.65

[a] [Monomer]/[metal] molar ratio. [b] Determined by GPC. [c] Determined by ^{13}C NMR using the carbonyl signals. [d] A 50-μL catalyst solution was used. [e] Precipitated into methanol and is the methanol-insoluble portion. [f] Precipitated into methanol and is the methanol-soluble portion. [g] Precipitated into petroleum ether and acetylacetone treated (see Experimental Section). [h] Unfractionated (UN) samples. [i] Sample showed a bimodal GPC trace (see Figure 2).

cipitated into methanol) or by decanting away the solvent (products precipitated into petroleum ether). The products prepared using Al- and Y-based catalysts were re-dissolved into acetyl acetate (AcAc, approximately 1 g of polymer per 10 mL of AcAc). The polymer AcAc solutions were then added to petroleum ether (1 to 10, v/v), and the mixtures were maintained at −20 °C for ~12 h and the supernatant was decanted to obtain the AcAc-treated insoluble products. All the polymer products were dried (50 °C, ~12 h, ~2 mmHg) prior to structural analysis.

Polymer Fractionation. PMPLs prepared by using IBAO and MAO as catalysts were fractionated using acetone as the solvent by Soxhlet extraction for ~16 h. The solvent was evaporated by a rotary evaporator to obtain the acetone-soluble (AS) PMPL. The AS fraction and the acetone-insoluble (AI) fraction remaining in the thimble were dried (50 °C, ~12 h, ~2 mmHg) prior to structural analysis.

Instrumentation. The molecular weights of the PMPLs were measured by gel permeation chromatography (GPC) using a Waters Model 510 pump, Model 410 refractive index detector, and Model 730 data module with 10^3-, 10^4-, 10^5-, and 10^6-Å Ultrastyragel columns in series. Chloroform was used as the eluent at a flow rate of 1.0 mL/min. The sample concentration and injection volume were 0.3% (w/v) and 150 μL, respectively. The molecular weights are relative to polystyrene standards. Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Varian Unity 300 operated at 75.4 MHz and 35 °C, and the chemical shifts in parts per million (ppm) were recorded using $CDCl_3$ as the reference at 77.00 ppm. The polymer solutions were approximately 4% (w/v) in $CDCl_3$. Experimental parameters for the ^{13}C NMR spectra were as follows: pulse width 9.7 μs; acquisition time 2 s; relaxation delay 1 s; 64K data points and 3000−4000 transients; line broadening −0.5; and Gaussian broadening 0.5. Differential scanning calorimetry (DSC) measurements were performed on a Du Pont 2910 DSC equipped with a TA 2000 data station, using approximately 5 mg of sample sealed in aluminum pans and a dry N_2 purge. The polymer samples were cooled to −70 °C and were heated at a rate of 10 °C/min to 140 °C, rapidly quenched from the melt using liquid N_2, and then analyzed during second heating scans from −70 to 140 °C. The data reported for peak melting temperature(s) (T_m) and enthalpy of fusion (ΔH_f) were taken from the first heat. Where multiple melting transitions were observed, the reported ΔH_f value was taken as the cumulative value over the entire melting transition range. The glass transition temperature (T_g) values were the midpoint values measured during the second heating scans.

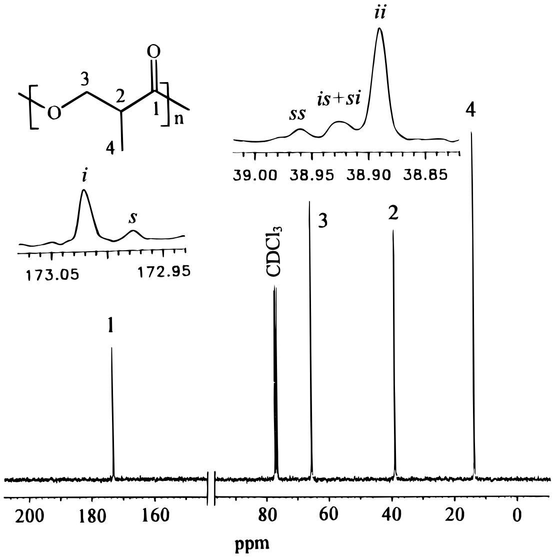

Figure 1. ^{13}C NMR 75.4-MHz spectrum of IBAO-AI prepared from racemic MPL using IBAO as the catalyst.

Results and Discussion

$Zn(C_2H_5)_2/H_2O$ (1/0.6)-Catalyzed MPL Polymerization. Previous work established that $Zn(C_2H_5)_2/H_2O$ (1/0.6)-catalyzed BL ring-opening polymerization proceeds with random (*R*)- and (*S*)-BL chain-propagation statistics.[3,13,21,35] However, $Zn(C_2H_5)_2/H_2O$ catalysts have shown isospecificity for propylene oxide polymerizations.[22] The polymerization conditions for $Zn(C_2H_5)_2/H_2O$ (1/0.6)-catalyzed MPL polymerization are given in Table 1 (see also Experimental Section) and are similar to those used previously for BL polymerization.[3,21] Our laboratory reported that the ^{13}C NMR signals of the carbonyl, methine, and methyl carbons of PMPL are sensitive to the chain sequence of the polymer backbone.[1] The fractions of isotactic (i) and syndiotactic (s) diads can be determined from the carbonyl or the methyl ^{13}C NMR signals, while the fractions of isotactic (ii), syndiotactic (ss), and heterotactic (is + si) triad stereosequences can be determined from the methine ^{13}C NMR signals. As an example, which is discussed below, the 75.4-MHz ^{13}C NMR spectrum of the acetone-insoluble PMPL fraction prepared using IBAO as catalyst (IBAO-AI product) along with expansions of the carbonyl and methine carbon signal regions is shown in Figure 1. The rationale for the assignment of diad and triad stereosequences was presented elsewhere.[1] The i-diad fractions of the products synthesized herein were measured by ^{13}C NMR using the expanded carbonyl signal region,[1] and the results are listed in Table 1. The polymerization of MPL using the $Zn(C_2H_5)_2/H_2O$ (1/0.6) catalyst system gave PMPL with an i-diad fraction of 0.51. The experimental diad and triad stereosequence fractions are in excellent agreement with that calculated using the Bernoulli model (triad results not shown). Thus, it is concluded that the $Zn(C_2H_5)_2/H_2O$ (1/0.6) catalyst system, under the polymerization conditions used herein, was nonstereoregulating, leading to random (*R*)- and (*S*)-MPL chain-propagation statistics. Moreover, the position on the β-propiolactone ring of the methyl substituent did not lead to an observable change in the stereospecificity of $Zn(C_2H_5)_2/H_2O$ (1/0.6)-catalyzed chain propagation. In a polymerization time of 7 days, the methanol-insoluble polymer yield was 55% and the product had a number-average molecular weight (M_n) and dispersity (M_w/M_n) of 22 200 and 1.44, respectively.

Polymerization using Sn-Based Catalysts. By $(^nC_4H_9)_3SnOCH_3$ catalysis, PMPL of low isotacticity with an i-diad fraction of 0.55−0.56 for both methanol-insoluble and -soluble fractions resulted (see Table 1). It appears that fractionation in methanol was caused by differences in product molecular weight since the methanol-insoluble fraction had a substantially higher M_n. $(^nC_4H_9)_2Sn(OCH_3)_2$-catalyzed polymerization of racemic MPL resulted in an atactic product having similar yield and molecular weight characteristics as that obtained using $(^nC_4H_9)_3SnOCH_3$. It is interesting to consider that use of these catalysts for polymerization of racemic BL resulted in syndio-regulation.[17,18] Thus, it is concluded that placement of the methyl substituent of the β-propiolactone ring at the α- instead of the β-position alters steric interactions between the incoming monomer and catalyst−chain end complex in such a way so that syndioaddition is no longer preferred.

Polymerization using Lanthanide- and Yttrium-Based Catalysts. The lanthanide compound $La(O^iC_3H_7)_3$ and $Y(O^iC_3H_7)_3$ were evaluated as catalysts for MPL polymerization carried out in bulk. During a reaction time of 21 days at 60 °C, $La(O^iC_3H_7)_3$ showed low activity such that no observable petroleum ether insoluble product was formed (see Table 1). However, $Y(O^iC_3H_7)_3$ displayed relatively higher activity such that for an monomer-to-catalyst ratio ([M]/[C]) of 50, the reaction reached gelation in approximately 4 h at 60 °C. After a 3-day reaction time, the yield of petroleum ether insoluble PMPL was 94% (see Table 1). Unfortunately, the product molecular weight was low (M_n = 3020 g/mol, M_w/M_n = 1.27). Higher MPL-to-$Y(O^iC_3H_7)_3$ ratios were studied in an effort to achieve higher product molecular weight. However, a polymerization with [M]/[C] = 1500 did not form any observable petroleum ether insoluble material after a 28-day reaction time. At [M]/[C] = 500, the polymerization proceeded slowly (41 days, 87% yield, see Table 1) to yield a product of increased M_n (11 000 g/mol). The relatively broad molecular weight distribution of PMPL products (M_w/M_n of 1.27−1.63) obtained using $Y(O^iC_3H_7)_3$ indicates that the polymerizations did not proceed via a living mechanism. ^{13}C NMR chain sequence analysis showed that the polymers obtained from $Y(O^iC_3H_7)_3$ at 60 °C have very low isotacticity, with i-diad fractions of 0.53−0.54. Decreasing the polymerization temperature to −20 °C did not lead to any observable increase in catalyst stereoregulation (see Table 1).

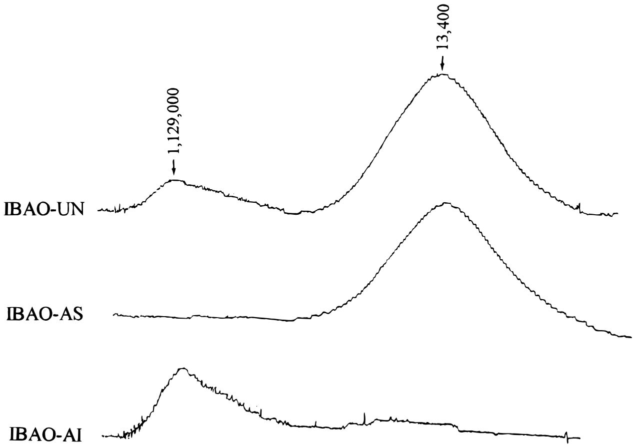

Figure 2. GPC chromatograms of IBAO-UN, IBAO-AS, and IBAO-AI prepared from racemic MPL using IBAO as the catalyst.

Polymerization using Al-based Catalysts. The results of MPL polymerizations using Al-based catalysts are also shown in Table 1. $Al(O^iC_3H_7)_3$ is an active catalyst for the polymerization of MPL such that for a 3-day polymerization at 60 °C and an [M]/[C] ratio of 50, the yield of petroleum ether insoluble PMPL was 95%. Similar results were obtained using $(C_2H_5)_2AlOC_2H_5$ as catalyst (see Table 1). The polymers formed by $Al(O^iC_3H_7)_3$ and $(C_2H_5)_2AlOC_2H_5$ catalysis were of relatively low molecular weight, as would be anticipated based on the correspondingly low [M]/[C] ratio used. Furthermore, the molecular weight distribution (M_w/M_n) values were 1.40 and 1.71, respectively, indicating that the polymerizations deviate from a living mechanism. These results differ largely from the polymerizations of ϵ-caprolactone, lactide, and β-(1,1-dichloroalkyl)-β-propiolactones using $Al(O^iC_3H_7)_3$ as catalyst, which are "living", leading to rather narrow molecular weight distributions and molecular weights which can be predicted based on the monomer-to-catalyst ratio.[26−33] Since in this work the ratio of monomer to catalyst was not varied and product molecular weights were measured relative to polystyrene, comparisons between experimental and calculated molecular weights will not be considered herein. As shown in Table 1, both the $Al(O^iC_3H_7)_3$ and $(C_2H_5)_2AlOC_2H_5$ catalysts were nonstereoregulating, leading to PMPL products with i-diad fractions of 0.50.

The oligomeric catalysts IBAO, EAO, and MAO have been used to obtain predominantly isotactic PHB (i-diad fractions >0.80) by fractionating the heterogeneous products based on acetone solubility.[14−16,34] Following the same methodology, IBAO and MAO were used to polymerize MPL, and the results are listed in Table 1. Similarly to the polymerization of BL using IBAO, IBAO catalyzed racemic MPL to form PMPL with a very broad molecular weight distribution (see Figure 2). The petroleum ether insoluble and AcAc-treated[13,14] product was fractionated by acetone extraction (see Experimental Section) into an acetone-insoluble fraction (IBAO-AI, 36% by weight) and an acetone-soluble fraction (IBAO-AS, 64% by weight) (see Table 2). The GPC chromatograms of the unfractionated sample (IBAO-UN), IBAO-AS, and IBAO-AI are shown in Figure 2. The IBAO-UN exhibits a bimodal GPC trace with high and low molecular weight peaks at 1129 000 and 13 400 g/mol, respectively. IBAO-AS showed only one peak which occurred at exactly the same elution volume as the lower molecular weight peak of IBAO-UN, while IBAO-AI showed a peak that centers at the same elution volume corresponding to the higher molecular weight

Table 2. Molecular Weight and Stereosequence Distribution Results from IBAO-Catalyzed Polymerization of Racemic MPL

			diad fract[c]		triad fract[d]			
sample[a]	wt %	M_n (M_w/M_n)[b] × 10^{-3}, g/mol	i	s	ii	ss	is + si	E[e]
IBAO-UN	100	6.85 (2.78)/641 (1.40)[f]	0.65	0.35	0.43 [0.47]	0.19 [0.18]	0.38 [0.35]	1.00
IBAO-AI	36	662 (1.35)	0.85	0.15	0.75 [0.77]	0.08 [0.08]	0.17 [0.15]	0.94
IBAO-AS	64	6.74 (2.61)	0.57	0.43	0.33 [0.35]	0.22 [0.22]	0.45 [0.43]	0.98

[a] UN, AI, and AS refer to the unfractionated product, acetone-insoluble fraction, and acetone-soluble fraction, respectively. [b] Determined by GPC. [c] Diad fractions were obtained from the carbonyl ^{13}C NMR signals. [d] Triad fractions were obtained from the methine ^{13}C NMR signals. Data in brackets were calculated from the diad fractions using the enantiomorphic model equations: $i = 1 - 2\alpha(1 - \alpha)$; $s = 2\alpha(1 - \alpha)$; $ii = 1 - 3\alpha(1 - \alpha)$; $ss = \alpha(1 - \alpha)$; $is + si = 2\alpha(1 - \alpha)$ (see refs 36−38). [e] Enantiomorphic model triad test, $E = 2(ss)/(is + si)$. $E = 1$ for a product formed by a polymerization which perfectly fits the model (see refs 36−38). [f] Sample showed a bimodal GPC trace (see Figure 2).

peak of IBAO-UN. Thus, acetone fractionation was effective in separating the high and low molecular weight components of IBAO-UN. The IBAO-AS or lower molecular weight fraction had M_n and M_w/M_n values of 6740 g/mol and 2.61, respectively. In contrast, the IBAO-AI fraction had M_n and M_w/M_n values of 662 000 g/mol and 1.35, respectively (see Table 2). The unfractionated, AS, and AI products from IBAO catalysis were also analyzed by 75.4-MHz ^{13}C NMR to determine the distribution of repeat unit stereosequences. The ^{13}C NMR spectrum of the IBAO-AI fraction is displayed in Figure 1 (see above). Analysis of this spectrum shows that IBAO-AI is predominantly isotactic, having an i-diad fraction of 0.85. The experimental diad and triad stereosequence fractions for IBAO-UN, IBAO-AI, and IBAO-AS are listed in Table 2. From Table 2, it is apparent that the IBAO-AS fraction is of low isotacticity (0.57 i diads). Thus, the PMPL product obtained from IBAO catalysis can be fractionated by acetone extraction into a high molecular weight and largely isotactic fraction and a fraction of relatively low i-diad content and molecular weight. Such a result is similarly observed for the IBAO-catalyzed polymerization of racemic BL.[14−16,34] The triad fraction values measured experimentally from the methine ^{13}C NMR signals are compared to that calculated (shown in brackets) using the enantiomorphic-site model[36−38] (see Table 2). The triad fractions from the enantiomorphic-site model are in good agreement with those obtained experimentally. Furthermore, the enantiomorphic-site model triad test (see legend *e* in Table 2 and refs 36−38) E values are close to 1.00, which further supports that this model accurately depicts the operative polymerization mechanism. Specifically, the enantiomorphic-site model assumes that the configuration of the adding monomer is primarily controlled by the configuration of the catalytic sites and the configuration of the chain end has a negligible effect. Hocking and Marchessault[38] have shown that the enantiomorphic-site model can well describe the isotactic PHB prepared from racemic BL using aluminoxanes as catalysts but not the atactic and syndiotactic PHB. Thus, it appears that both isotactic PHB and PMPL prepared from racemic BL and MPL, respectively, using aluminoxanes as catalysts can be described by the enantiomorphic-site model.

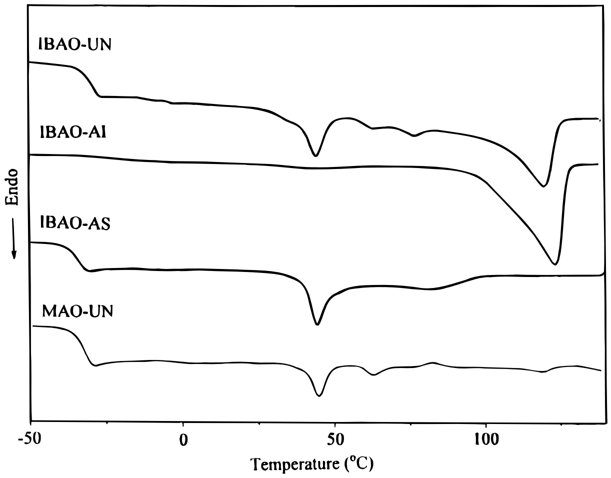

Figure 3. DSC first heating scan thermograms of IBAO-UN, IBAO-AI, IBAO-AS, and MAO-UN.

Table 3. Thermal Analysis by DSC of PMPL Products formed by IBAO- and MAO-Catalyzed Polymerization of Racemic MPL

sample	T_g,[a] (°C)	T_m[b] (°C)	ΔH_f,[c] (cal/g)
IBAO-UN	−30	44, 60, 76, **120**	6.5
IBAO-AI	−25	123	16.3
IBAO-AS	−33	**44**, 84	3.8
MAO-UN	−32	**44**, 62, 119	1.5

[a] Obtained from second heating scans. [b] Obtained from the first heating scans. Bold T_m values where multiple melting transitions were observed are the melting temperatures which correspond to the largest component endotherm transition. [c] Calculated over the entire range of sample melting.

The thermal transitions of the PMPL fractions obtained from IBAO-catalyzed MPL polymerization were studied by DSC. Figure 3 shows the first heating scans of the IBAO-UN, IBAO-AI, IBAO-AS, and MAO-UN samples. The results from Figure 3 are compiled in Table 3. The first heating scan of IBAO-UN shows two major melting endotherms with peak temperatures (T_m) at 44 and 120 °C, respectively. The enthalpy of fusion (ΔH_f) over the entire melting range of the sample is relatively low (6.5 cal/g, see below). The IBAO-AS and IBAO-AI fractions have dominant endotherm T_m values at 44 and 123 °C, respectively. Moreover, the IBAO-AS and IBAO-AI fractions have ΔH_f values of 3.8 and 16.3 cal/g, respectively (see Table 3). Thus, in agreement with the results presented above, acetone fractionation resulted in a largely isotactic AI fraction which, by virtue of its stereoregularity, appears highly crystalline by DSC. This is supported by the fact that PMPL having 90% (*R*) repeat units prepared from (*R*)-enriched MPL had a T_m, ΔH_f, and degree of crystallinity of 130 °C, 20.8 cal/g, and 73%, respectively.[1] The second heating scans of the samples (thermograms not shown) reveal that the T_g value for IBAO-AI is considerably higher than that for IBAO-AS (−25 and −33 °C, respectively). This difference in T_g may result from the higher molecular weight of the former sample. However, on the basis of a previous investigation with PMPL stereoisomers of almost identical chain length,[1] we believe that the relatively high T_g value of the IBAO-AI sample is due in part to increased chain rigidity, corresponding to largely isotactic chain sequences.

The polymerization of MPL using MAO as the catalyst resulted in PMPL of relatively low molecular weight ($M_n = 4740$, $M_w/M_n = 2.53$). This product was fractionated by acetone extraction. Unlike the polymerization of BL using MAO as the catalyst, no observable AI fraction was obtained from this PMPL product. DSC analysis of the unfractionated PMPL sample (MAO-UN) during the first heating scan showed that there were small melting endotherms with T_m values of 44, 62, and 119 °C and the ΔH_f over the entire melting region was 1.5 cal/g (see Figure 3 and Table 3). Thus, the MAO catalyst did not lead to a substantial high molecular weight and largely isotactic fraction. It is noteworthy that the melting temperatures of MAO-UN at 44 and 119 °C are very close to those of IBAO-UN (44 and 120 °C). However, the content of the largely isotactic PMPL corresponding to the high melting temperature formed by MAO is much less than that using IBAO based on the ΔH_f values. Thus, it is concluded that the MAO and IBAO catalysts both have catalytic sites capable of producing largely isotactic and low isotacticity PMPL. However, the relative number or the activity of the isoregulating catalytic sites in the IBAO catalyst is considerably greater.

It has been suggested for the polymerization of racemic BL using aluminoxane catalysts that the catalysts contain at least two types of catalytic sites which produce isotactic PHB of high molecular weight and atactic PHB of low molecular weight.[15,16] Recent studies have further extended these conclusions since a small yield of low molecular weight (typical $M_n \cong 600$ g/mol) predominantly syndiotactic PHB (s-diad fractions up to 0.68) was isolated from the product obtained by MAO-catalyzed racemic BL polymerization.[19] The presence of drastically different catalysis mechanisms by different catalytic sites in aluminoxane polymerizations resulting in polymer fractions of variable tacticity is consistent with the observation that both acyl and alkyl ring-opening mechanisms were operative in BL polymerization catalyzed by ethylaluminoxane.[21] The isotatic catalytic sites were claimed to have a higher ratio of rates for chain propagation to chain termination and/or chain transfer than that of atactic catalytic sites.[16] Based on our observations for MPL polymerization by MAO and IBAO catalysis, these conclusions appear applicable to the present system, except that a high molecular weight product was not isolated from MAO-catalyzed polymerization.

Conclusion

Polymerizations of racemic MPL using the $Zn(C_2H_5)_2/H_2O$ (1/0.6), $(^nC_4H_9)_2Sn(OCH_3)_2$, $Al(O^iC_3H_7)_3$, and $(C_2H_5)_2AlOC_2H_5$ catalyst systems resulted in atactic PMPL, while $(^nC_4H_9)_3SnOCH_3$ and $Y(O^iC_3H_7)_3$ gave PMPL of low isotacticity with isotactic diad fractions between 0.53 and 0.56. $La(O^iC_3H_7)_3$ did not show substantial activity for the polymerization of MPL over a reaction period of 21 days. The PMPL products obtained from the active catalysts above had molecular weight distributions between 1.26 and 1.71. The corresponding M_n values were relatively low (1810 to 22 200 g/mol), but in some cases, such as when using $Al(O^iC_3H_7)_3$ and $(C_2H_5)_2AlOC_2H_5$, the product molecular weights may be limited by the monomer-to-catalyst ratio investigated. The aluminoxane catalyst IBAO was effective for the preparation of highly isotactic PMPL. GPC, DSC, and ^{13}C NMR analyses on product fractions separated based on their solubility in acetone showed that the PMPL sample formed using the IBAO-catalyst is heterogeneous in composition. Specifically, the IBAO catalyzed product contained an acetone-insoluble fraction that was of high molecular weight and high isotacticity and an acetone soluble fraction of relatively low molecular weight and low isotacticity. The acetone-insoluble fraction was highly crystalline based on DSC analysis and comparisons to results on thermal properties for (*R*)-enriched PMPL products. MAO gave distinctly different results than IBAO-catalyzed MPL polymerization. Specifically, the number or activity of catalytic sites that lead to highly isotactic PMPL was less for MAO than for IBAO. However, the general behavior of IBAO catalyzed BL and MPL polymerizations was similar. Specifically, IBAO catalysts contain at least two types of catalytic sites which produce a largely isotactic fraction with high molecular weight and a low isotacticity fraction with low molecular weight.

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